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## Seasonal and diel variation of atmospheric mercury concentrations in the Reno (Nevada, USA) airshed

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#### Abstract

This paper describes total gaseous mercury (TGM) concentrations measured in Reno, Nevada from 2002 to 2005. The 3-year mean and median air Hg concentrations were 2.3 and 2.1 ng m<sup>-3</sup>, respectively. Mercury concentrations exhibited seasonality, with the highest concentrations in winter, and the lowest in summer and fall. A well-defined diel pattern in TGM concentration was observed, with maximum daily concentrations observed in the morning and minimum in the afternoon. A gradual increase of TGM concentration was observed in the evening and over night. The early morning increase in TGM was likely due to activation of local surface emission sources by rising solar irradiance and air temperature. The subsequent decline and afternoon minimum in TGM were likely related to increased vertical mixing and the buildup of atmospheric oxidants during the day resulting in increased conversion to oxidized species that are quickly deposited, coupled with weakening of the surface emissions processes. The described diel pattern was seasonally modulated with the greatest amplitude in variation of TGM concentrations occurring in the summer. It is suggested based on the comparison of diel TGM pattern with other gaseous pollutants that natural source surface emissions are a dominant source of TGM in the study area.

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#### 1. Introduction

The cycling and behavior of Hg are functions of its chemical form in the atmosphere. Atmospheric Hg is predominantly (~95%) found in the gaseous elemental (Hg<sup>0</sup>) form (Lindberg and Stratton, 1998), which has a relatively long estimated global atmospheric lifetime (4 months–1 year; Schroeder and Munthe, 1998). A smaller fraction (about 3%, Lindberg and Stratton, 1998) is made up of gaseous

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Hg(II) species (reactive gaseous mercury, RGM) which are thought to be deposited quickly (Lin and Pehkonen, 1999; Schroeder and Munthe, 1998), and Hg associated with airborne particles (Hg<sub>p</sub>). In the atmosphere, Hg<sup>0</sup> may be transformed to RGM through gas and aqueous phase oxidation reactions involving oxidants such as ozone (O<sub>3</sub>), hydroxyl (\*OH), hydroxyl peroxyl (HO<sub>2</sub>), and alkyl peroxy (RO<sub>2</sub>) radicals, H<sub>2</sub>O<sub>2</sub>, NO<sub>3</sub>, and halogens (Ariya et al., 2004; Lin and Pehkonen, 1999; Pal and Ariya, 2004; Schroeder et al., 1991). Of these, O<sub>3</sub> is most routinely monitored as part of ambient air quality monitoring across the US as one of six major air pollutants regulated by the Clean Air Act (US EPA,

2006). Although there is some disagreement, most published reaction rates for direct oxidation of Hg<sup>0</sup> with O<sub>3</sub> are slow (Bergan and Rodhe, 2001; Biswajit and Parisa, 2003; Pal and Ariya, 2004). A variety of other photochemical oxidants are typically associated with O<sub>3</sub> (Finlayson-Pitts and Pitts, 1997; Sillman, 2003). For example, increased 'OH concentrations might be expected when concentrations of O<sub>3</sub> are higher as photolysis of O<sub>3</sub> is a major source of OH (Shao et al., 2004). In turn, oxidation of organic compounds by 'OH and O<sub>3</sub> produces peroxyl radicals (Finlayson-Pitts and Pitts, 1997; Shao et al., 2004; Sillman, 1999). Because of these relationships and the fact that only O<sub>3</sub> data were available for the study area, O<sub>3</sub> concentrations are used in this paper as a surrogate measure of oxidizing potential of the atmosphere.

The average global atmospheric Hg concentration in the lower troposphere is approximately  $1.5-2.0 \,\mathrm{ng}\,\mathrm{m}^{-3}$  (Ebinghaus et al., 2001, 2002), with somewhat higher concentrations (range 2.0-4.1 ng m<sup>-3</sup>) reported for urban air (Dommergue et al., 2002; Gabriel et al., 2005; Landis et al., 2002b; Lynam and Keeler, 2005; Nadim et al., 2001; Péchevran et al., 2000). However, few long-term air Hg concentration measurement data sets are available from urban areas in the western hemisphere (cf. Nadim et al., 2001), while results of longterm atmospheric Hg speciation measurements have started to emerge only recently (Poissant et al., 2005; Yatavelli et al., 2006). Air Hg concentrations measured at a point could be influenced by natural and anthropogenic sources. Factors thought to be most important in controlling Hg emissions from natural sources are light (Gustin et al., 2002), temperature (Poissant et al., 1999; Schluter, 2000; Zhang and Lindberg, 1999), and soil moisture (Gustin and Stamenkovic, 2005; Poissant et al., 1999), with episodic spikes in emissions pronounced after precipitation (Lindberg et al., 1999). Besides anthropogenic point sources, mobile sources (e.g., cars, trucks, buses) may contribute to atmospheric Hg in an urban setting.

This paper adds to the database of long-term ambient Hg concentrations in urban areas. Ambient Hg concentrations measured from summer 2002 to summer 2005 in the semi-arid urban airshed of Reno (Nevada, USA) are analyzed for an overall trend, on a seasonal time step, and for diel variability. Environmental parameters and available ambient air quality data, and a limited air Hg speciation dataset (colleted in summer 2005) are

used in this paper to guide in interpreting observed temporal patterns of air Hg concentration.

#### 2. Methods

#### 2.1. Site description

Total gaseous Hg in the Reno airshed was monitored from August 2002 to August 2005 at the Desert Research Institute (DRI). The DRI (39°34′N, 119°48′W, elevation 1509 m) is located on a hill at the northern edge of Reno, Nevada (USA). Reno is an urban area (population ca. 200,000) in a semi-arid valley between the Sierra Nevada and Virginia mountain ranges, located at 1340 m above sea level. The DRI is situated in an area of hydrothermally altered (argillic) andesite flows, near the historic Wedekind Mining District which contains gold, silver and mercury deposits (Garside and Schilling, 1979; IAMLETF, 1999). The naturally Hg-enriched Steamboat Springs geothermal area (site of the Nevada STORMS project, Gustin et al., 1999; Lindberg et al., 1999; Poissant et al., 1999) is located approximately 20 km south of DRI. A gasdiesel fired power plant is located 27 km east of downtown. Thus, air Hg concentrations in the Reno airshed are potentially impacted by local natural and anthropogenic sources. Longer-range transport of pollutants from upwind cities in California (e.g. Sacramento and San Francisco) is also possible.

Average daily temperatures are mild, but daily maxima and minima can differ by as much as 25 °C. Annual precipitation averages 190 mm with more than 50% occurring from December to March. Humidity is very low during the summer months (daily average 38%, afternoon average 20%), and moderately low during the winter (65% and 47% daily and afternoon averages, respectively). Reno has wintertime inversions that can strongly affect air quality and chemistry (Keislar, 1993), while during summer the boundary layer height is very high, allowing for strong vertical mixing associated with urban areas in arid climates (Grossman-Clarke et al., 2005).

#### 2.2. Mercury measurements

A Tekran<sup>®</sup> 2537A Mercury Vapor Analyzer (Tekran Inc., Toronto, Canada) was used to monitor air Hg concentrations. It has been demonstrated that under low air humidity conditions the Tekran 2537A quantifies total gaseous Hg (TGM = GEM + RGM)

in ambient air (Temme et al., 2003). The instrument detection limit is  $< 0.1 \text{ ng m}^{-3} \text{ using the } 2.5\text{-min}$ sampling intervals, which were applied in this study (Tekran Inc., 1999). Air was sampled every 10 min from two ducts bringing in the ambient air from outside the Fritz Vent Greenhouse at DRI (air intakes for the two ducts are located 1 m above ground, approximately 35 m apart). Particulate matter was removed by a 45-mm Teflon® filter (0.2 µm pore size) at the beginning of the sampling line. All tubing and connections were made of acidcleaned PTFE that were checked for contamination before measurements commenced. Between sampling intervals, the tubing was continuously flushed to prevent stagnant air. The system was checked for contamination monthly by including a Tekran<sup>®</sup> 1100 Zero Air Generator (Tekran Inc., Toronto, Canada) or a zero-air canister at the end of the sampling line. No contamination was detected for the duration of the study. The analytical quality control consisted of daily internal perm source standard injections into ambient air using a Tekran® 1120 Standard Addition unit (Tekran Inc., Toronto, Canada), and automated daily calibrations in Hg-free air. In addition, the accuracy of the instrument was periodically compared with other Tekran 2537A analyzers, and was verified by manual injections of a known volume of air from a saturated mercury vapor source at a known temperature into ambient air. When recoveries dropped below 90%, the gold cartridges inside Tekran 2537A were cleaned or replaced to achieve efficiency of 95% or better. The instruments were not adjusted for daylight savings time.

Mercury speciation sampling took place atop a 20-m tower approximately 180 m west from the Fritz Vent Greenhouse in summer 2005. A Tekran 2537A-1130-1135 automated mercury speciation system was used for sequential collection of GEM, RGM, and Hg<sub>p</sub> (Landis et al., 2002a). The flow rate into the Model 2537A was  $11 \mathrm{min}^{-1}$ , with the total flow through the KCl-coated quartz annular denuder and quartz filter assembly of  $71 \mathrm{min}^{-1}$  (Lyman et al., 2007). The system inlet, tubing, glassware, and other components were cleaned or replaced regularly.

# 2.3. Environmental parameters and gaseous pollutants

Hourly averaged meteorological parameters (wind speed and direction, solar radiation, air

temperature, relative humidity, barometric pressure and precipitation) were collected at the DRI's Western Regional Climate Center weather station.

Ozone,  $NO_x$ , CO, and particulate matter ( $PM_{10}$ ) concentrations used for statistical analyses were measured at a Washoe County District Health Department Air Quality Management Division station located in downtown Reno (elevation 1340 m), approximately 5 km south of DRI. These air quality data were compared with those measured at another monitoring station (elevation 1585 m), 9 km northwest of DRI. Ozone and CO concentrations measured at the two stations were almost identical over the study period (linear regression slope of 1.1,  $r^2 = 0.96$ ), indicating that spatial distribution of pollutants was nearly uniform across the area. Since DRI is located between these two monitoring stations, the air quality data may be compared with air Hg concentrations measured at DRI.

### 2.4. Data analysis

No data points were excluded based on statistical criteria only (e.g. outliers exceeding mean + 3 SD). Instead, abnormally high TGM concentrations were omitted only if persisting less than 2h and not observed in both ducts (considered to be a result of disturbance in the immediate vicinity of the air intake). Daily averaged TGM concentrations were used to analyze longer-term patterns (overall trend, monthly and seasonal variability). Composite hourly averages of TGM derived using 3 years of data were used to examine the diel variability in TGM. Data were managed and manipulated using Stata® Statistical Software (Release 6.0 for Windows, StataCorp, College Station, Texas). All analyses were performed using MINITAB® Statistical Software (Release 13.32 for Windows, State College, Pennsylvania) and considered significant at p < 0.05.

#### 3. Results and discussion

#### 3.1. General trends in TGM

A total of 1095 days of TGM concentration measurements were collected from August 2002 to August 2005 (8% of data lost due to calibrations, equipment malfunctions and maintenance, or other use of the Tekran 2537A). The 3-year mean and median TGM concentrations were 2.3 and

 $2.1 \text{ ng m}^{-3}$ , respectively (range  $0.9-8.6 \text{ ng m}^{-3}$ ). n = 279,537). The linear trend analysis (Fig. 1) of average daily TGM concentrations resulted in a slope of  $-0.00013 \,\mathrm{ng}\,\mathrm{m}^{-3}\,\mathrm{day}^{-1}$ , equivalent to an annual decrease of approximately 2% when compared to the overall average value (accuracy measures of the fitted trend: MAPE = 21.86, MAD = 0.47, MSD = 0.46, p = 0.059). Omitting the periods with lower TGM in summers of 2002 and 2005 (denoted by asterisks in Fig. 1) resulted in an improved fit and significant trend (MAPE = 18.73,MAD = 0.45. MSD = 0.42. p < 0.001) and suggested a decreasing trend of  $0.00035 \,\mathrm{ng}\,\mathrm{m}^{-3}\,\mathrm{day}^{-1}$ . However, derived decreasing trends should be viewed with caution due to the limited length of the available time series.

The observed TGM concentrations during the 3 years of the study were higher than the Northern Hemisphere background concentrations of 1.5–2.0 ng m<sup>-3</sup> (Ebinghaus et al., 2001), but within the 2.0–4.1 ng m<sup>-3</sup> range reported for urban air in the US and Europe (Dommergue et al., 2002; Gabriel et al., 2005; Landis et al., 2002a; Lynam and Keeler, 2005; Nadim et al., 2001; Pécheyran et al., 2000).

Over 3 years, only 20 episodes (lasting 1–7 days) with elevated Hg concentrations (average daily TGM above 3.5 ng Hg m<sup>-3</sup>) were observed (Fig. 1). Although detailed source apportionment (e.g. receptor modeling) was beyond the scope of this work, the potential for correlations between

environmental conditions (precipitation, wind speed and direction, atmospheric pressure, air temperature and humidity, solar irradiance) and air chemistry (concentrations of gaseous pollutants) was examined in detail for the elevated TGM events. Approximately a third of these episodic spikes in TGM concentrations were following precipitation events (denoted by a in Fig. 1), which contribute to increased emissions (Lindberg et al., 1999). Elevated CO, NO<sub>x</sub>, O<sub>3</sub> or PM<sub>10</sub> concentrations were recorded during some of the high TGM events (b in Fig. 1), indicating possibility of pollution plumes arriving in the airshed, or occurrence of inversions and accumulation of gaseous pollutants. Some events could not be attributed to any measured parameter (d in Fig. 1), implicating a combination of fluctuations of a variety of meteorological and emission variables.

#### 3.2. Seasonal variability

Although concentrations of TGM were variable throughout the year, the mean was greater for winter months (Table 1). Air concentrations of gaseous pollutants also exhibited seasonality (Fig. 2), with maximum  $NO_x$  and CO concentrations in winter, and  $O_3$  maximum in summer.

Winter maxima in atmospheric Hg concentrations have been observed at some background sites (Blanchard et al., 2002; Ebinghaus et al., 2002; Kellerhals et al., 2003; Kim et al., 2005; Kock et al.,

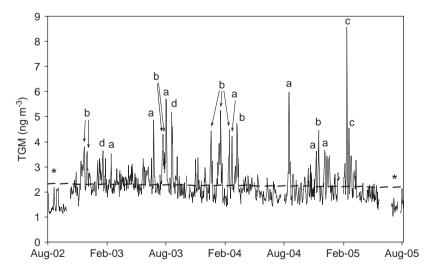


Fig. 1. Time series plot of average daily concentrations of TGM measured at Desert Research Institute (Reno, Nevada) from 2002 to 2005. Fitted trend equation for all data: y = 2.3-0.00013t (in days). Letters indicate potential sources/causes of elevated TGM (a) following precipitation), atmospheric signature of pollution plumes (b), elevated NO<sub>x</sub>, CO or PM<sub>10</sub> concentrations), marked change in meteorological conditions (c), change in barometric pressure), or no specific indicator (d). Asterisks denote periods of unusually low TGM.

2005: Slemr, 1996), and have been suggested to be related to seasonal differences in combustion of fossil fuels, atmospheric oxidant concentrations, mixing layer depth and meteorological conditions. Likewise, higher NO<sub>x</sub> and CO concentrations in winter may be both due to increased source strength, and due the presence of wintertime temperature inversions, as well as weakening atmospheric sinks (oxidants). Ozone reached maximum concentrations in summer when solar irradiance and air temperatures are the highest, as is commonly observed for oxidants that are secondary pollutants due to the photochemistry involved (Warneck, 2000). In addition to lower boundary layer height, lower oxidant concentration and lower rate constants for oxidation reactions at lower temperatures (Hewitt and Harrison, 1985) could contribute to seasonal modulation of the pollutant sink strength, resulting in high CO and NO<sub>x</sub> concentrations in winter.

#### 3.3. Diel variability and weekly patterns

Composite hourly averages derived using 3 years of data revealed a regular pattern with maximum TGM concentrations in mid morning and minimum concentrations in the afternoon (Fig. 3). The observed daily pattern was seasonally modulated.

The interval between daily maxima and minima was on average 2 h longer in summer than in winter, related to the day length change. The magnitude of diel variation (difference between daily maxima and minima) was the greatest in summer (0.8 ng m<sup>-3</sup>, corresponding to 37% when referred to the summer average concentration) and the smallest in winter (0.3 ng m<sup>-3</sup>, 12% difference when compared to the winter average).

Long-term air Hg concentration measurements from Seoul, South Korea (Kim and Kim, 2001; Kim et al., 2005; Shon et al., 2005), Chinese cities of Guiyang (Feng et al., 2003, 2004) and Changchun (Fang et al., 2004), and in a suburban area in France (Dommergue et al., 2002) also revealed regular diel patterns with high Hg concentrations in the morning and mid-afternoon depletion. Shon et al. (2005) suggested that nighttime buildup of atmospheric Hg in Seoul was due to use of fossil fuels, long-range transport and natural sources, while reaction with ozone was identified as a dominant sink.

 $NO_x$  and CO exhibited peak concentrations in the morning, while  $O_3$  concentration peaked during and after the maximum solar irradiance (Fig. 4). Diel  $NO_x$  and CO concentration patterns are similar to those observed in other areas, and are typically associated with the morning commute emissions into thin boundary layer (cf. Touma et al., 2006),

Table 1
Summary of seasonal<sup>a</sup> means±standard deviation (first row) and medians (second row) of average daily TGM concentrations and meteorological parameters measured at the Desert Research Institute from August 2002 to August 2005

	Spring	Summer	Fall	Winter
TGM (ng m <sup>-3</sup> )	$2.2 \pm 0.4$ $2.2$	$2.2 \pm 0.8$ $2.0$	$2.1 \pm 0.5$ 2.0	$2.5 \pm 0.8$ $2.3$
Total solar radiation $(kWhm^{-2})$	$5.3 \pm 1.4$ $5.2$	$6.8 \pm 1.1$ $7.1$	$3.6 \pm 1.5$ $3.5$	$2.1 \pm 0.8$ 2.2
Temperature (°C)	$10.1 \pm 5.2$ 9.8	$22.9 \pm 3.3$ $23.2$	$11.8 \pm 7.5$ $11.8$	$2.3 \pm 3.7$ 2.4
Humidity (%)	$42 \pm 14$ $41$	$26 \pm 11$ 23	$38 \pm 19$ 32	$66 \pm 14$ $67$
Total precipitation (mm)	$28\pm4$	$31\pm13$	$40 \pm 36$	$49\pm23$
Wind speed (m s <sup>-1</sup> )	$3.0 \pm 1.0$ $2.8$	$2.7 \pm 0.5$ $2.6$	$2.3 \pm 0.9$ 2.0	$2.1 \pm 1.0$ $1.8$
Wind direction <sup>b</sup> (°)	$286\pm72$	295±51	$17\pm93$	$53\pm95$
Pressure (mb)	848±5 847	849±3 849	849±5 850	$849 \pm 6$ $850$

<sup>&</sup>lt;sup>a</sup>Spring: March–June, summer: July–August, fall: September–November, and winter: December–February (cf. Kim et al., 2005).

<sup>&</sup>lt;sup>b</sup>Average wind direction was computed using circular statistics (Zar, 1999; Mardia and Jupp, 2000).

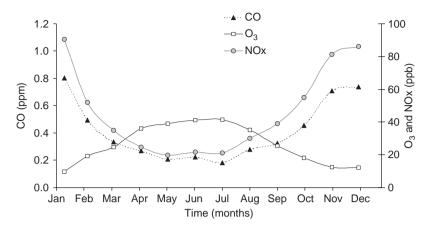


Fig. 2. Monthly variations of mean concentrations of carbon monoxide (CO), nitrogen oxides (NO $_x$ ) and ozone (O $_3$ ) in Reno from 2002 to 2005.

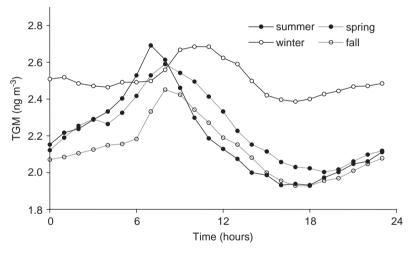


Fig. 3. Hourly averaged TGM concentrations by season (spring: March–June, summer: July–August, fall: September–November, winter: December–February) derived using data from 2002 to 2005.

while daily minimum in the afternoon is due to dilution as convective mixing increases later in the day, and due to removal by oxidation (Sillman, 2003). Typical of oxidants that are secondary pollutants and commonly appear to anticorrelate with the precursor species and peak in the early afternoon (Sillman, 2003; Warneck, 2000), the diel pattern in  $O_3$  concentration was the opposite of those of  $NO_x$  and CO (in the Reno area the majority of  $O_3$  precursors come from motor vehicles; Washoe County District Health Department, 2004). With respect to days of week, weekends had the lowest morning peaks of CO and  $NO_x$  (Fig. 4), confirming that sources of these pollutants are dominated by vehicular emissions, as weekdays exhibit busier

morning rush hour patterns than weekends. Higher  $O_3$  concentrations are notable on weekends (paired  $t=7.77,\ p<0.001$ ), hypothesized to be linked to lower CO and  $NO_x$  emissions on weekends that reduces the titration of ozone (cf. Atkinson-Palombo et al., 2006). In turn, the increased oxidizing capacity of the atmosphere on weekends may result in a decrease in other trace gas concentrations on those days.

Hourly averaged TGM concentrations were positively correlated with NO<sub>x</sub> ( $y = 7.0 \text{ NO}_x$  in ppm + 1.9;  $r^2 = 0.59$ , p < 0.001) and CO (y = 0.6 CO in ppm + 2.0;  $r^2 = 0.37$ , p < 0.001), and although TGM was anticorrelated with O<sub>3</sub>, this relationship was not statistically significant. Due to the strong

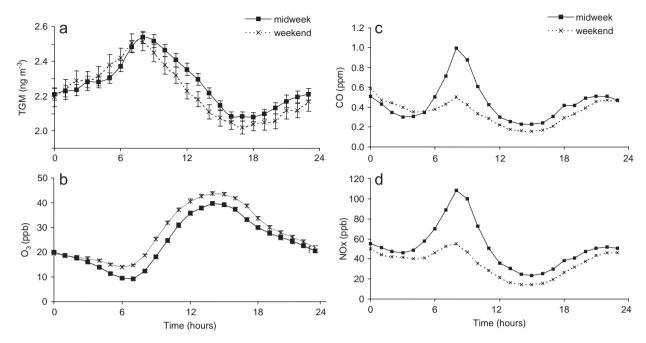


Fig. 4. Hourly averaged concentrations of all data from 2002 to 2005 by mid week (Monday–Friday) and weekend (Saturday and Sunday) of (a) TGM, (b) ozone (O<sub>3</sub>), (c) carbon monoxide (CO) and (d) nitrogen oxides (NO<sub>x</sub>).

similarity of TGM diel variability and NO<sub>x</sub> and CO concentrations, we hypothesize that removal mechanisms during the day are similar for these pollutants, such as dilution with the deepening of the boundary layer in the afternoon, and oxidation by 'OH, O<sub>3</sub>, and peroxy radicals from photochemical reactions (Prinn, 2003; Sillman, 2003). During the night the stability of the boundary layer increases, trapping TGM emitted from various sources, and leading to a gradual nighttime increase in TGM concentration.

Morning peaks in TGM concentrations were not weekday dependent (Fig. 4), while afternoon TGM concentrations were significantly lower during the weekend than at the same time on weekdays (paired t = -3.22, p = 0.004, average difference  $70-120 \text{ pg m}^{-3}$ ). Contrary to NO<sub>x</sub> and CO, no difference in mid-morning peak concentrations of TGM between weekdays and weekends suggests that air Hg sources in the Reno airshed are likely dominated by natural surface emissions (e.g. from Hg enriched substrate) rather than vehicular emissions. Furthermore, the vertical mixing height alone cannot account for the observed difference in TGM since the depth of boundary layer is not weekday dependent, suggesting the existence of a daytime sink that is stronger on weekends. One possible afternoon sink for TGM are daytime atmospheric oxidants. Increased oxidizing capacity on weekends (see above) could lead to an increased conversion of GEM to RGM species that are then rapidly deposited, resulting in an overall decrease of TGM.

# 3.4. Mercury speciation: a case study in summer 2005

Mercury species measured 20 m above ground at DRI from June to August 2005 are summarized in Table 2. Concentrations of GEM measured at 20 m exhibited a diel pattern similar to TGM concentrations measured in air duct of the Fritz Vent Greenhouse, with the gradient (TGM measured at 1 m less than GEM measure at 20 m) indicating deposition during most of the day, except mid morning (Fig. 5).

Average daily maxima for RGM and Hg<sub>p</sub> during the case study at DRI were 72 and  $18 \,\mathrm{pg}\,\mathrm{m}^{-3}$ , respectively. Overall, RGM peaked in the early afternoon (Fig. 5), and hourly averaged concentrations were positively correlated with solar irradiance in kW m<sup>-2</sup> (y = 25.7x + 28.7;  $r^2 = 0.54$ , p < 0.001), air temperature in °C (y = 1.8x - 6.5;  $r^2 = 0.52$ , p < 0.001), and O<sub>3</sub> concentration in ppb (y = 0.6x + 14.9;  $r^2 = 0.49$ , p < 0.001), and anticorrelated with relative humidity in % (y = -0.9x + 58.7;  $r^2 = 0.51$ , p < 0.001). Hourly averaged Hg<sub>p</sub> concentrations

Table 2 Statistical summary of Hg speciation measured at the Desert Research Institute from June to August 2005

	Mean	SD	$SE^a$	Median	25th percentile	75th percentile	n
GEM (ng m <sup>-3</sup> )	1.6	0.5	0.01	1.5	1.3	1.8	8082
$RGM (pg m^{-3})$	37	28	2	30	16	52	286
$\mathrm{Hg_p}\ (\mathrm{pg}\mathrm{m}^{-3})$	7	9	1	6	3	9	285

<sup>&</sup>lt;sup>a</sup>SE, standard error of mean (SD/square root of N).

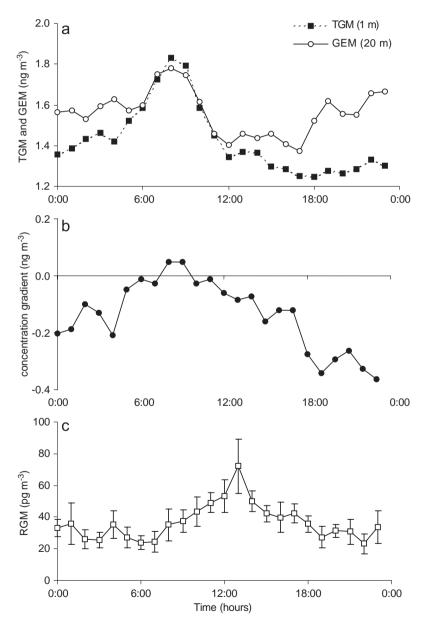


Fig. 5. (a) Hourly averaged gaseous elemental (GEM) and total gaseous mercury (TGM); (b) average concentration gradient during day (TGM measured at 1 m less GEM measured at 20 m above ground); and (c) hourly means ± SE of reactive gaseous mercury (RGM) measured from June to August 2005 at DRI.

were weakly but significantly (p<0.05) positively correlated with air temperature, solar irradiance and ozone, and anticorrelated with relative humidity, but simple linear regressions only accounted for 18–22% of the observed variability in Hg<sub>p</sub> concentrations.

The occurrence of early afternoon maxima in RGM concentrations have been observed elsewhere (Lynam and Keeler, 2005; Lindberg and Stratton, 1998) and this pattern is similar to diel variability reported for atmospheric oxidant concentrations (Warneck, 2000). Daily maxima in RGM and Hg<sub>n</sub> concentrations in this study corresponded well with the differences in afternoon TGM concentrations between weekdays and weekends (70–120 pg m<sup>-3</sup>, Fig. 4). This seems to support the hypothesis that afternoon declines in TGM observed at the study site were not only due to changes in vertical mixing, but also due to oxidation of GEM and subsequent deposition of oxidized Hg species. The general gradient pattern is also consistent with the activation of natural surface emissions in the morning with sunrise and increased temperatures (Gustin et al., 2002; Poissant et al., 1999; Schluter, 2000; Zhang and Lindberg, 1999), and deposition later in the day.

#### 4. Conclusions

Concentrations of TGM in the Reno airshed showed a slight decreasing trend from 2002 to 2005. Intra-annual variability included elevated TGM in winter compared to summer periods, and a regular diel pattern with mid-morning peaks and afternoon minima that was seasonally modulated. The diel variability of TGM could largely be explained by the thickness of the boundary layer, based on comparison with other gaseous pollutants and other work. However, two marked characteristics of TGM in the study area were observed. Contrary to gaseous pollutants with sources dominated by vehicular emissions, TGM sources appeared to be dominated by natural emission sources. This is supported by the lack of weekday dependence of observed diel variability of TGM, concentration gradient measured at two heights, and by the effect precipitation had on the average daily TGM concentrations. Secondly, the diurnal pattern of TGM was affected by atmospheric oxidants, as illustrated by afternoon TGM concentration differences on weekdays and weekends, and by afternoon

peaks in concentrations of oxidized Hg and correlation between RGM and  $O_3$ .

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